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Specifications

1. Title of Invention:

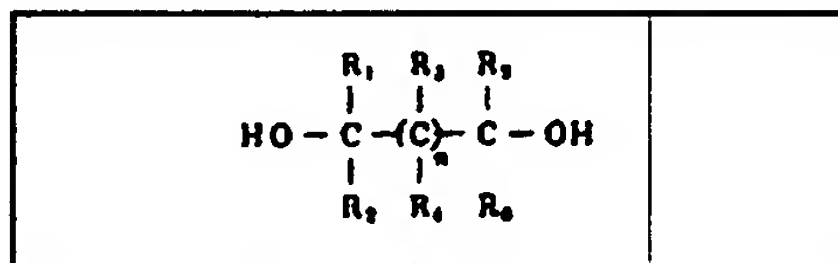
Process for producing synthetic leather

2. Claims:

A process for producing synthetic leather, characterized in that, in a process for producing synthetic leather which is formed from an urethane resin surface layer, an emulsion resin mechanical foam layer, and a substrate, the urethane resin used in said surface layer is a high-molecular urethane resin the principal ingredients of which are a polyhydroxy compound, an organic isocyanate, and a chain-extending agent, and the chain-extending agent used is a diol compound with one or more alkyl groups on its side chains, shown by general formula (A):

(A)

(wherein n is an integer in the range of 1–6; R₁, R₂, R₃, R₄, R₅, and R₆ are alkyl groups with carbon of 1–4; and at least one of the groups R₁–R₆ is an alkyl group).



range of 1–6; R₁, R₂, hydrogen atoms or numbers in the range the groups R₁–R₆ is an

3. Detailed Explanation of Invention:

This invention concerns a process for producing synthetic leather with an excellent external appearance and a flexible feel, resembling that of natural leather. In particular, it concerns a process for producing synthetic leather with an excellent external appearance which has an emulsion resin mechanical foam layer, and in which the low-molecular surface active agent contained in the foam layer does not bleed on the surface.

In general, as is well known, synthetic leathers consist of a surface layer, an adhesive layer, and a substrate, etc.; they are obtained by forming a urethane resin surface layer on a mold release material, adhering a 2-liquid-type urethane resin to the substrate as an adhesive, and then peeling the mold release material off. In recent years, furthermore, in order to obtain synthetic leathers with external appearances and feels which resemble natural leather more closely, synthetic leathers have been produced industrially which have a foam layer between the urethane resin surface layer and the substrate. Methods for introducing the foam layer include:

(1) the method of spreading a urethane resin dissolved in a hydrophilic solvent on a substrate or support and then treating the result in an aqueous solvent in which the urethane resin is insoluble (wet foaming method);

(2)the method of producing a foam by using carbon dioxide gas produced by the reaction of the isocyanate group and water (isocyanate dry foaming method); and

(3)the method of producing a foam by adding a blowing agent which produces a suitable degree of gas by being heated (blowing agent dry foaming method).

The wet foaming method, however, has a number of problems, including the waste water disposal problem, the complexity of the process, and the high production cost. The dry foaming methods can be performed by applying conventional processes, but they have the drawback that they are very easily influenced by temperature and humidity, so that production using these methods is unstable.

Therefore, methods have been investigated recently for applying mechanical foam layers of emulsion resins to synthetic leathers, using conventional equipment, as a method for obtaining foam layers in a stable and inexpensive manner.

Mechanical foaming of emulsion resins is publicly known as a mechanical foam technology which uses acrylic resins, synthetic rubber latexes, natural rubber latexes, vinyl chloride resin emulsions, ethylene vinyl acetate resin emulsions, urethane resin emulsions, etc., and it is widely used for carpet backing, light-blocking curtains, etc. These emulsion resins are made by stirring emulsions mechanically and dispersing air in the emulsion in fine [bubbles]; therefore, a low-molecular surface active agent is generally used as the blowing agent.

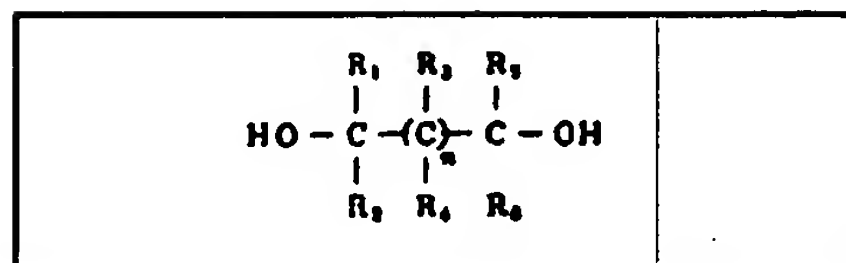
Ammonium oleate is generally used with natural rubber and synthetic rubber latexes, and ammonium stearate shows a good foaming activity in vinyl chloride resin emulsions, acrylic resin emulsions, urethane resin emulsions, etc. Furthermore, extremely fine bubbles are obtained, and they are stable when heated and dried after they are applied to the support, with little destruction of the bubbles. In addition, the foam layers obtained have smooth surfaces, and they are uniformly fine.

Synthetic leathers which have surface layers obtained by using these foam layers have flexible feels and external appearances with small creases, very closely resembling natural leather.

However, the synthetic leather obtained in this way has the drawback that the blowing agent, which is a low-molecular surface active agent, bleeds to the surface of the synthetic leather as a fine white powder when the synthetic leather is placed in a high-temperature, humid place for a long time, or immersed in water. This bleeding phenomenon harms the external appearance and greatly reduces the commercial value of the synthetic leather.

The inventors performed careful research to improve these drawbacks. As a result, they discovered that they could be improved by using a polyurethane resin obtained by using certain diol compounds as chain-extending agents in a method for producing synthetic leathers consisting of a surface layer, an emulsion resin mechanical foam layer, and a substrate; these diol compounds have one or more alkyl groups on their side chains, as shown by general formula (A):

(A)



(wherein n is an integer in the range of 1-6; R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are hydrogen atoms or alkyl groups with carbon numbers in the range of 1-4; and at least one of the groups R_1 - R_6 is an alkyl group). In this manner, they arrived at this invention.

The urethane resins used in the surface layer of this invention are produced by suitably combining polyethers or polyesters, etc., with linear structures which have hydroxyl groups on both ends with organic diisocyanates and the diol compounds shown by the general formula given above as chain-extending agents and synthesizing the urethane resins in solvents which are inert with respect to isocyanates, e.g., dimethylformamide or methyl ethyl ketone.

The organic diisocyanates used in synthesizing the urethane resins are aromatic, aliphatic, or alicyclic diisocyanates which have been in common use for a long time. They include 2,4- and 2,6-tolylene diisocyanate (TDI), 4,4-diphenylmethane diisocyanate (MDI), 1,5-naphtylene diisocyanate (NDI), xylylene diisocyanate (XDI), dicyclohexylmethane-4,4-diisocyanate (HMDI), 3-isocyanate methyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI), 1,6-hexamethylene diisocyanate (HDI), and 2,6-diisocyanate methyl caproate (LDI), which may be used either individually or in mixtures.

Examples of polyhydroxy compounds with hydroxyl groups on both ends which react with these organic diisocyanates are polyether polyols, polyester polyols, polycaprolactone polyols, polyester ether copolymer polyols, etc., with mean molecular weights of 600-3000. Desirable examples of the polyether polyols are polyalkylene ether polyols, such as polypropylene ether glycol, polytetramethylene ether polyol, etc. As the polyester polyols, polyesters obtained by polycondensing diol compounds such as ethylene glycol, propylene glycol, butylene glycol, neopentyl glycol, 1,6-hexadiol, diethylene glycol, dipropylene glycol, etc., either individually or in mixtures, with dibasic acids, e.g., adipic acid, maleic acid, succinic acid, phthalic acid, isophthalic acid, fumaric acid, or acid esters of these acids. It is desirable to obtain the polycaprolactone polyols by the ring-opening polymerization of caprolactone to the aforementioned diol compounds. These hydroxy compounds may be used individually or in mixtures of two or more.

The chain-extending agents used in this invention are not especially limited; they may be any diol compounds with one or more alkyl groups in their side chains which are shown by general formula (A) above. However, it is desirable to use, for example, 1,2-propylene glycol, in which $n=0$ and R_1 is a methyl group; pinacol, in which $n=0$ and R_1 , R_2 , R_5 , and R_6 are methyl groups; neopentyl glycol, in which $n=1$ and R_3 and R_4 are

methyl groups; and 1,3-butanediol, in which $n=1$ and R_1 is a methyl group. These compounds are easily produced industrially, or are supplied inexpensively in large quantities. Furthermore, the chain-extending agents used in this invention can be used individually, but in some cases they can also be used together with other publicly known chain-extending agents. Examples of chain-extending agents which can be used together with these agents are linear aliphatic glycols, such as ethylene glycol, 1,4-butanediol, 1,6-hexanediol, etc., and alkanolamines, such as ethanolamine, propanolamine, etc.

If these agents are used together with the ones of this invention, the ratio of the chain-extending agents of this invention, shown in general formula (A) above, and the other chain-extending agents is in the range of 10:1–1:9, preferably 10:0–5:5.

The production of the urethane resins used in the surface layer of this invention is not especially limited; one may use ones produced by any conventional, publicly known methods.

For example, they may be produced by a one-step process, in which all of the ingredients are mixed at once, from the beginning, in a solvent which is a good solvent of urethane resins but is inert with respect to the isocyanate group, or they may be produced by a process in which a urethane prepolymer is synthesized, after which the chain of the urethane prepolymer is extended in a solvent to increase its molecular weight. In this case, the chain-extending agents of this invention may be used by themselves as the chain-extending agent, or other chain-extending agents which are already publicly known may be used in addition.

The proportion in which the chain-extending agents are used varies with the mean molecular weights of the polyhydroxy compounds with hydroxyl groups on both ends (polyesters, polyethers, etc.) as well as with the molecular weights of the chain-extending agents used. When a resin with a certain feel or a certain stress characteristic is being designed, this proportion is determined by the number average molecular weight of the whole diol compound when the polyhydroxy compound and the chain-extending agents are mixed.

Considering the urethane resins which can be used in the surface layer of the synthetic leather (the emulsion mechanical foam), their number average molecular weights are in the range of 200–1000 ; if it is less than 200, the urethane resins are extremely hard, and if it is greater than 1000, they are soft, but they have a strong surface tackiness, which causes problems in their use. Desirable number average molecular weights are in the range of 300–600.

Examples of the emulsion resins in the emulsion mechanical foam layer used in this invention are ones which are ordinarily known in the emulsion industry, such as polyvinyl chloride emulsions, natural rubber latexes, synthetic rubber latexes, ethylene-vinyl acetate emulsions, acrylic emulsions, urethane emulsions, etc., either individually or in mixtures of two or more. Acrylic and urethane emulsions are especially desirable as materials for artificial leather.

The resin concentration of the emulsion for mechanical foaming should be in the range of 50–60 wt%.

The mechanical foam layer is obtained by adding foaming agents, col ring agents, cross-linking agents, cross-linking catalysts, thickeners, and, if desired, fillers, etc., to these emulsions, after which these compositions are vigorously stirred mechanically so that air is mixed into them in a fine manner, and they are foamed to 1.5–5 times their original volume. After this, the foam is coated on a support, dried, and heat-treated.

Examples of foaming agents which can be used are alkali metal salts, ammonium salts, amine salts, etc., of higher fatty acids, such as palmitic acid, stearic acid, behenic acid, etc. By using them as the foaming agents of the emulsion, extremely fine bubbles are obtained, and at the same time the bubbles are stable during the coating and drying processes; they are indispensable as foaming agents for acrylic or urethane emulsions. They may be used individually or in combinations of two or more; furthermore, they may also be used together with higher alcohols, higher alcohol sodium sulfates, higher fatty acid amide alkyl sodium sulfonates, etc. The quantity of these agents which is added to the emulsion is in the range of 1–15 wt% of the emulsion. For example, it is desirable to add ammonium stearate at 1–5.0 wt% of the emulsion.

Even if the quantity of these higher fatty acid salts added is small, they pass through the surface layer of the synthetic layer and cause a bleeding phenomenon if the synthetic leather is left for long periods of time in high-temperature, high-humidity conditions, or in hot water, etc. The surface of the leather becomes white, and its commercial value is markedly reduced.

As the cross-linking agents, one can use ones which are generally used in the industry, e.g., methylol melamine, methylol ethylene urea, methylol urea, and their initial condensates, etc.; if desired, one can also use catalysts which are ordinarily used, e.g., organic amine or metal catalysts. One can also use epoxy resins, e.g., an emulsion of an epoxy resin synthesized from bisphenol A and epichlorohydrin, or polyglycidyl ether compounds of aliphatic polyols, such as ethylene glycol, propylene glycol, glycerol, trimethylol propane, etc. If desired, they can also be used together with amine hardeners, such as aliphatic polyamines, aromatic amines, etc., which are well known in the industry.

The quantity of these cross-linking agents added is in the range of 2–15 wt%, preferably 3–8 wt%, of the emulsion resin. Furthermore, the catalysts or hardeners are added in suitable quantities, according to the kinds used and the heat treatment conditions.

The emulsion must have a suitable viscosity in order to form the emulsion mechanical foam layer; considering the suitability of the emulsion for the coating process, it should be in the range of 5,000–50,000 ps, preferably 8,000–20,000 ps. The viscosity is adjusted to the desired value by adding a thickener.

As thickeners, one can use water-soluble polymers or alkali-soluble acrylic acid emulsions; for example, one can use methyl cellulose, carboxymethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid copolymer emulsion, etc. Polyacrylic acid copolymer emulsion is preferable, since the thickening effect can be easily obtained by adding only a small quantity of it.

In addition, one can use coloring agents obtained by dispersing pigments in water

and fillers, such as calcium carbonate, clay, and talc.

The substrate of the synthetic leather may be weaves or nonwoven fabrics made from natural fibers, reconstituted fibers, or synthetic fibers, such as cotton, rayon, nylon, esters, etc., and surface nap may be raised on them.

The methods for producing the synthetic leather may be classified into two categories, transfer methods, using mold release supports, and direct coating methods, in which direct application to the substrate is performed. Either of these kinds of methods can be used to accomplish the desired purpose.

As an example of a transfer method, a urethane resin based on this invention is applied to a mold release paper at 50–300 g/m² wet and dried for 1–5 min at a temperature of 50–120°C, to form a film 5–30 mm thick. A foaming agent, cross-linking agent, thickener, etc., are compounded with the emulsion, and air is finely mixed with it mechanically to produce a foam emulsion, which is foamed to 2–5 times the original volume and applied on top of the surface layer obtained in this way at 50–500 g/m² wet. After the result is dried for 2–100 min at a temperature of 50–150°C, the substrate is placed on it, pressed, and heat-treated for 2–10 minutes at 50–150°C to dry it. After cooling, the mold separation paper is peeled off. Or, the foamed emulsion resin is applied to the mold separation paper on which the surface layer has been formed, and a heat treatment to dry it is performed for 2–10 min at a temperature of 50–150°C, after which an adhesive is applied to the foam layer or the substrate, the layers are adhered together, and drying and cooling are performed. After this, the mold separation paper is peeled off. Moreover, if necessary, after the mold separation paper is peeled off, patterning of the surface layer may be performed by gravure printing, etc.

As an example of a direct coating method, a foaming agent, cross-linking agent, cross-linking catalyst, hardener, thickener, and in some cases, a coloring agent, filler, etc., are compounded with an emulsion resin, and air is finely mixed with it mechanically to produce a foam emulsion resin which is foamed to 2–5 times the original volume. This foam emulsion resin is applied directly on a substrate, or on a substrate which has been treated to make it water-repellant obtained in this way, at 100–1000 g/m² wet. Drying is performed by performing a heat treatment at 50–150°C for 2–10 minutes, to form a foam layer. After this, the urethane resin produced on the basis of this invention is applied on the foam layer at 30–200 g/m² wet, and drying is performed at 50–120°C for 1–5 minutes, to obtain a synthetic leather. If necessary, the surface touch can also be modified by applying acrylic, amino acid, alcohol-soluble polyamide, etc., resins on top of this synthetic leather. Furthermore, an external appearance resembling natural leather can be produced by including a process of patterning by using an embossing roller or a rubbing¹ process.

The synthetic leather obtained by using the material of this invention is extremely

¹ May also mean "crumpling" – Translator's note

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soft and has a volume feeling. In addition, it has an external appearance resembling natural leather. Furthermore, the synthetic leather obtained does not show the phenomenon of bleeding of the foaming agent even when it is left under high-temperature, high-humidity conditions for a long time or immersed in water, so that a synthetic leather with a high product value can be obtained.

This invention will be explained below by giving working examples, but it is not limited to these examples. Furthermore, the parts referred to in the working examples are parts by weight.

Working Example 1

One hundred fifty parts polytetramethylene adipate with a molecular weight of 2,000, 35 neopentyl glycol, and 3 parts 4,4'-diphenylmethane diisocyanate 101 were reacted at 75–85°C in a nitrogen gas stream and in dimethylformamide. As the viscosity rose, dimethylformamide was added; by the end of the reaction, 668 parts dimethylformamide was added. A uniform, transparent urethane resin for the surface layer, with a resin concentration of 30% and a viscosity of 500 ps (20°C), was obtained. Urethane resin for surface layer

The surface layer was formed by adding 20 parts coloring agent and 20 parts methyl ethyl ketone (as a diluting solvent) to 100 parts of the urethane resin for the surface layer obtained above and stirring and defoaming were performed until the mixture became uniform. After this, the mixture was applied to mold release paper (Sanririsu AR-22, Asahi Rouru Co.) at 100 g/m² wet, and drying was performed at 120°C for 3 minutes to form a surface layer.

Five parts Sumitekkusu Resin M-3 (methylol melamine, Sumitomo Chemical Industries Co.) (as a cross-linking agent), 0.5 part Sumitekkusu Accelerator ACX (amine catalyst, Sumitomo Chemical Industries Co.), 5 parts ammonium stearate (as a foaming agent), and 2 parts polyvinyl pyrrolidone (30% aqueous solution) (as a thickener) were added to and compounded with 50 parts Nikazouru FX-455 (acrylic emulsion, Nippon Carbide Industries Co.) (as an emulsion resin for the foam layer) and 50 parts Rezamin W (urethane emulsion, Dainichiseika Color and Chemicals Industry Co.). These ingredients were mixed with a mayonnaise mixer to foam them 2.8-fold. The result was applied on top of a mold release paper on which the surface layer previously produced had been formed, and a knit cloth was immediately placed on top of this layer and compressed. Drying was performed at 50°C for 5 minutes, and a heat treatment was performed at 150°C for 3 minutes. After cooling, the mold release paper was peeled off, and a flexible synthetic leather for apparel, with an appearance resembling natural leather, was obtained.

This synthetic leather was left for 2 months in a state of 70°C and 95% RH; no bleeding phenomenon was observed.

Working Example 2

The mold release paper on which a surface layer was formed in Working Example

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1 was used. As the emulsion resin for the foam layer, 5 parts trimethylol propane triglycidyl ether (as a cross-linking agent), 2 parts diethylenetriamine (as a hardener), 2.5 parts ammonium behenate (25% product) (as a foaming agent), 2.5 parts stearyl alcohol sodium sulfate, and 3 parts acrylic acid copolymer emulsion (as a thickener) were compounded with 100 parts Nikazouru FX-457 (acrylic emulsion, Nippon Carbide Industries Co.) (as an emulsion resin for the foam layer). These ingredients were mixed with a mayonnaise mixer to foam them 2.0-fold. The result was applied on top of a mold release paper on which the surface layer previously produced had been formed, and a napped cotton cloth was placed on top of this layer and compressed. Drying was performed at 100°C for 5 minutes, and a heat treatment was performed at 120°C for 2 minutes. After cooling, the mold release paper was peeled off, and a rubbing [*or* “*crumpling*” – *Translator*] and graining process was performed. As a result, a synthetic leather for bags with small creases, with an appearance resembling natural leather, was obtained. This synthetic leather was immersed for 3 hours in 20°C water, but no bleeding phenomenon was observed.

Working Example 3

One hundred parts polyethylene adipate with a molecular weight of 2,000, 50 parts polytetramethylene ether glycol, 15 parts neopentyl glycol, 5 parts 1,4-butanediol, and 74.3 parts 4,4'-diphenylmethane diisocyanate were weighed and reacted at 75–85°C in a nitrogen gas stream in dimethylformamide. As the viscosity rose, the mixture was diluted with dimethylformamide and methyl ethyl ketone; by the end of the reaction, a composition of dimethylformamide:methyl ethyl ketone=70:30 solvent was achieved. A uniform, transparent urethane resin for the surface layer, with a resin concentration of 30% and a viscosity of 400 ps (20°C), was obtained.

The surface layer was formed by adding 15 parts Seika Seven E Color (batch coloring agent, Dainichi Seika Color and Chemicals Industry Co.) and 30 parts methyl ethyl ketone (as a diluting solvent) to 100 parts of the urethane resin for the surface layer obtained above and stirring and defoaming were performed until the mixture became uniform. After this, the mixture was applied to mold release paper (Sanririsu AA-22, Asahi Rouru Co.) at 120 g/m² wet, and drying was performed at 110°C for 3 minutes to form a surface layer.

Five parts ammonium stearate (25% product) (as a foaming agent), 6 parts bisphenol A epoxy emulsion (60% product) (as a cross-linking agent), 2 parts tetraethylene pentamine (as a foaming agent), and 3 parts acrylic acid copolymer emulsion (35% product) (as a thickener) were added to 100 parts Rezamin W (urethane emulsion, Dainichiseika Color and Chemicals Industry Co.) (as an emulsion resin for the foaming layer). This mixture was foamed 2.3-fold with a mayonnaise mixer. The result was applied on top of a mold release paper on which the surface layer had been formed, and a nylon tricot was immediately placed on top of this layer and compressed. Drying was performed at 100°C for 5 minutes, and a heat treatment was performed at 120°C for 2 minutes. After cooling, the mold release paper was peeled off, and a flexible synthetic

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leather for apparel, with soft feel, was obtained.

Working Example 4

Five parts ammonium stearate (25% product) (as a foaming agent), 2 parts stearic acid amide alkyl sodium sulfonate (20% product), 3 parts Sumitekkusu Resin M-3 (methylol melamine, Sumitomo Chemical Industries Co.), 2 parts pentaerythritol triglycidyl ether, 1 part triethylenetetramine (as a hardening catalyst), 2 parts Seika Seven W Color (coloring agent, Dainichiseika Color and Chemicals Industry Co.) (as a coloring agent), 10 parts calcium carbonate (as a thickener), and 2 parts polyvinyl pyrrolidone (30% aqueous solution) (as a thickener) were added to and compounded with 50 parts Rezamin W (urethane emulsion, Dainichiseika Color and Chemicals Industry Co.) 50 parts Nikazouru FX-455 (acrylic emulsion, Nippon Carbide Industries Co.) (as emulsion resins for the foam layer). These ingredients were mixed with a mayonnaise mixer to foam them 3.5-fold. The result was applied on top of a weave of Tetron/rayon=35/65, which had been previously treated with a silicon or fluorine water repellant to make it water-repellant, at 300 g/m² wet. Drying was performed at 50°C for 7 minutes, and a heat treatment was performed at 135°C for 3 minutes. In this way, a foam layer was formed on the substrate.

Fifteen parts Seika Seven UST Color (coloring agent, Dainichiseika Color and Chemicals Industry Co.) (as a coloring agent) and 30 parts methyl ethyl ketone (as a diluting solvent) were added to 100 parts of the urethane resin for the surface layer produced in Working Example 3, and stirring and defoaming were performed until the mixture became uniform. After this, it was applied at 80 g/m² wet on the substrate on which the foam layer had been formed, and a urethane finishing agent was applied by gravure printing. After drying, a rubbing [or "crumpling" –Translator's note] process was performed, and a synthetic leather for bags with a volume feel was obtained. This synthetic leather was left for 2 months in a 70°C, 95% RH state, but no bleeding phenomenon was observed.

Working Example 5

Five parts ammonium stearate (as a foaming agent), 3 parts trimethylol propane diglycidyl ether (as a cross-linking agent), 3 parts Sumitekkusu Resin M-3 (methylol melamine, Sumitomo Chemical Industries Co.), 0.3 part Sumitekkusu Accelerator ACX (amine catalyst, Sumitomo Chemical Industries Co.), and 2.5 parts acrylic acid copolymer emulsion (35% product) (as a thickener) were added to and compounded with 100 parts Rezamin W (urethane emulsion, Dainichiseika Color and Chemicals Industry Co.), as an emulsion resin for foaming. These ingredients were mixed with a mayonnaise mixer to foam them 1.9-fold. The result was applied on top of a mold release paper on which the surface layer obtained in Working Example 1 had been formed at 200 g/m² wet. Drying was performed at 50°C for 5 minutes, and a heat treatment was performed at 130°C for 3 minutes; in this way a foam layer was formed. Furthermore, a two-solution urethane adhesive, which is already known in the industry, was applied at 100 g/m² wet,

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and a cotton knit was immediately pressed on top of this; drying was performed at 120°C for 3 minutes. After cooling, the mold release paper was peeled off, and a synthetic leather, with excellent flexibility, was obtained.

Comparison Example

For comparison with Working Examples 1–5, a urethane resin for a surface layer was synthesized as described below; other wise, the same method as in Working Examples 1–5 was used to produce an emulsion foam synthetic leather. A comparison bleeding test was performed, and the results are shown in Table 1.

Synthesis of surface layer urethane resin for comparison test

One hundred fifty parts polytetramethylene adipate with a molecular weight of 2,000, 12 parts 1,4-butanediol, and 52.1 parts 4,4'-diphenylmethane diisocyanate were weighed and reacted at 75–85°C in a nitrogen gas stream in dimethylformamide. As the viscosity rose, dimethylformamide was added; by the end of the reaction, 500 parts dimethylformamide had been added. A uniform, transparent surface layer urethane foam for performing the bleeding comparison test, with a resin concentration of 30% and a viscosity of 580 ps (20°C), was obtained. Furthermore, the comparison test was performed with synthetic leathers produced by the same methods as in the various working examples, using this surface layer. Comparison Examples 1, 2, 3, 4, and 5 correspond to Working Examples 1, 2, 3, 4, and 5.

Table 1

Table 1		
Bleeding test conditions	Left for 2 months at 70°C, 95% RH	Left for 3 hours in 20°C water
Sample		
Working Example 1	O	O
" 2	O	O
" 3	O	O
" 4	O	D
" 5	O	O
Comparison Example 1	D	X
" 2	D	X
" 3	D	X
" 4	X	X
" 5	D	X

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Evaluation standards:

O: No bleeding observed at all

O: Gloss of surface slightly changed

D: Bleeding observed clearly

X: Considerable amount of bleeding observed

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